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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) [redacted] 05 Mar 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-055**
Brent D. Viers (AFRL/PRSM); Joseph Mabry (ERC); Capt. Rene I. Gonzalez (AFRL/PRSM), "POSS is Not Just a Sphere: Fluorinated POSS Materials (Living Next Door to a Fluorine Chemist)"

American Chemical Society Conference **(Statement A)**
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 24 Feb 2003 – PAST DUE)

Personal Christe Anecdote

DISTRIBUTION STATEMENT A
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Living next door to a Fluorine Chemist

POSS is not just a sphere

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DISTRIBUTION STATEMENT A
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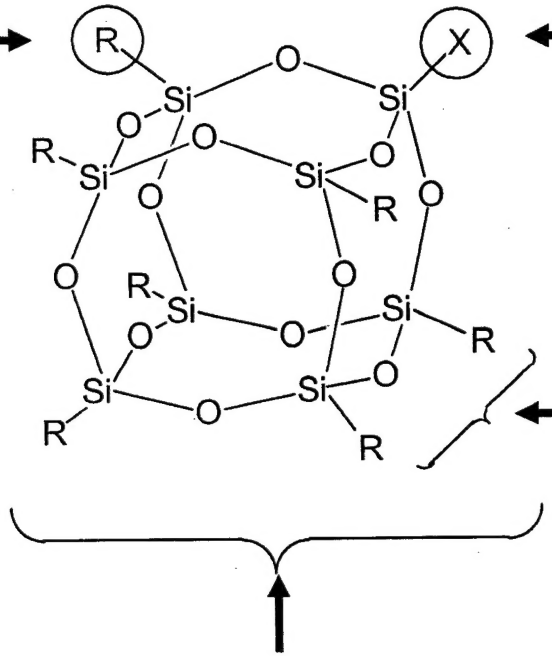
Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS) Molecule

Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

Physical properties of fluorinated Materials

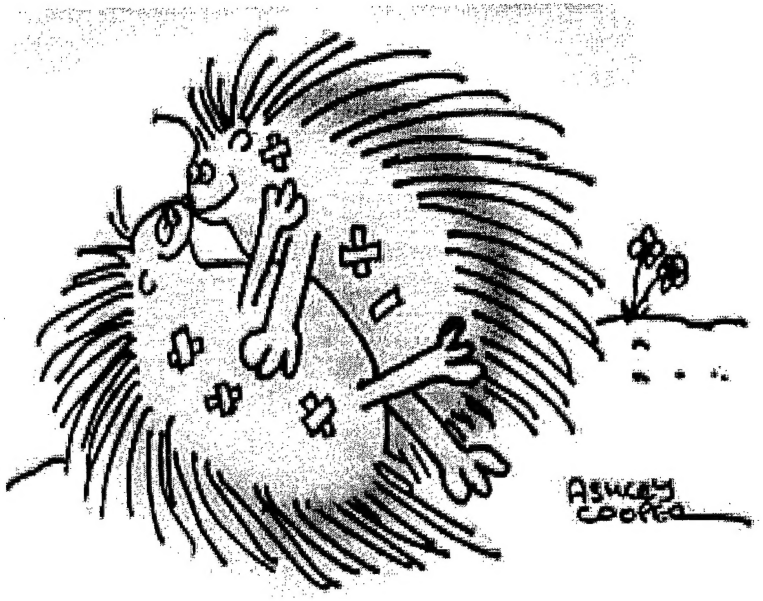
Property	Polytetra-fluoroethylene	Polyethelyne
Density	2.2–2.3	0.92–1
Melting Temperature, °C	342 (first) 327 (second)	105–140
Dielectric Constant (1 kHz)	2.0	2.3
Dynamic Coefficient of Friction	0.04	0.33
Surface Energy, dynes/g	18	33
Resistance to Solvents and Chemicals	Excellent. No known solvent	Susceptible to hot hydrocarbons
Thermal Stability[1] $T_{1/2}$, °C k_{350}, %/min E_{act}, kJ/mol	 505 0.000002 339	 404 0.008 264
Melt Viscosity, [2] Poise	10^{10}-10^{12}	10^4-6×10^4
Refractive Index	1.35	1.51
Chain Branching Propensity	No	Yes

[1] $T_{1/2}$ is the temperature at which 50% of the polymer is lost after thirty minutes heating in vacuum; k_{350} is the rate of volatilization, i.e., weight loss, at 350°C; E_{act} is the activation energy of thermal degradation.

[2] Melt creep viscosity for PTFE at 380°C, as specified in US Patent 3,819,594 (pub. 6/25/74).

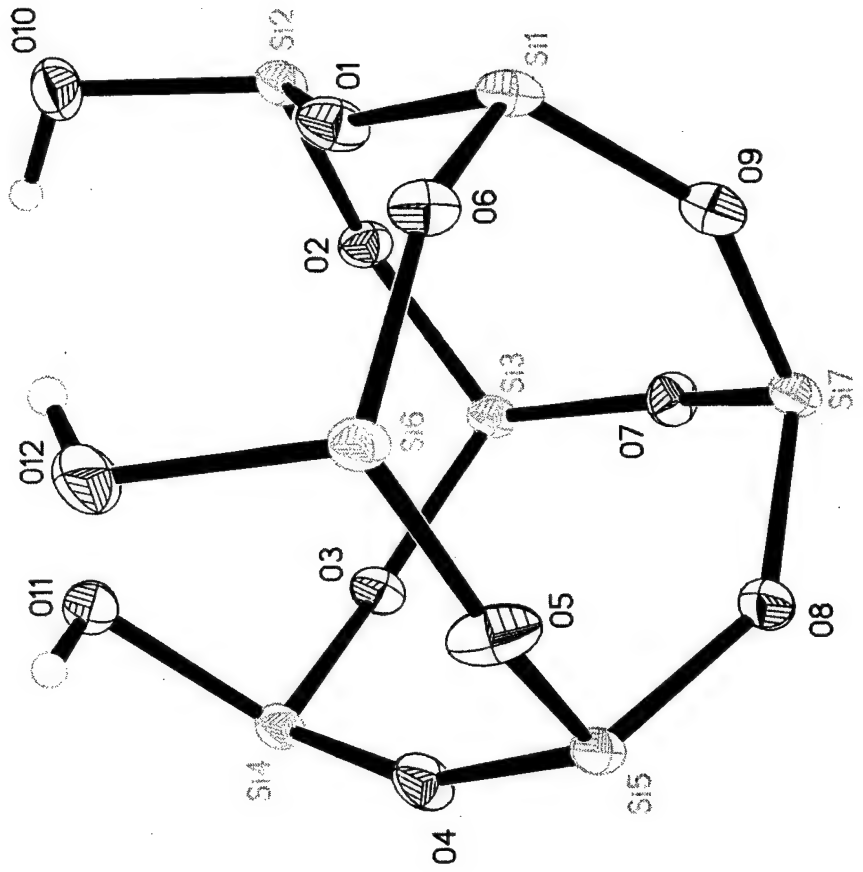
1. PTFE has one of the lowest surface energies among the organic polymers
2. PTFE is the most chemically resistant organic polymer
3. PTFE is one of the most thermally stable among organic polymers
4. PTFE's melting point and specific gravity are more than double PE's

How do Porcupines Mate



Very carefully!

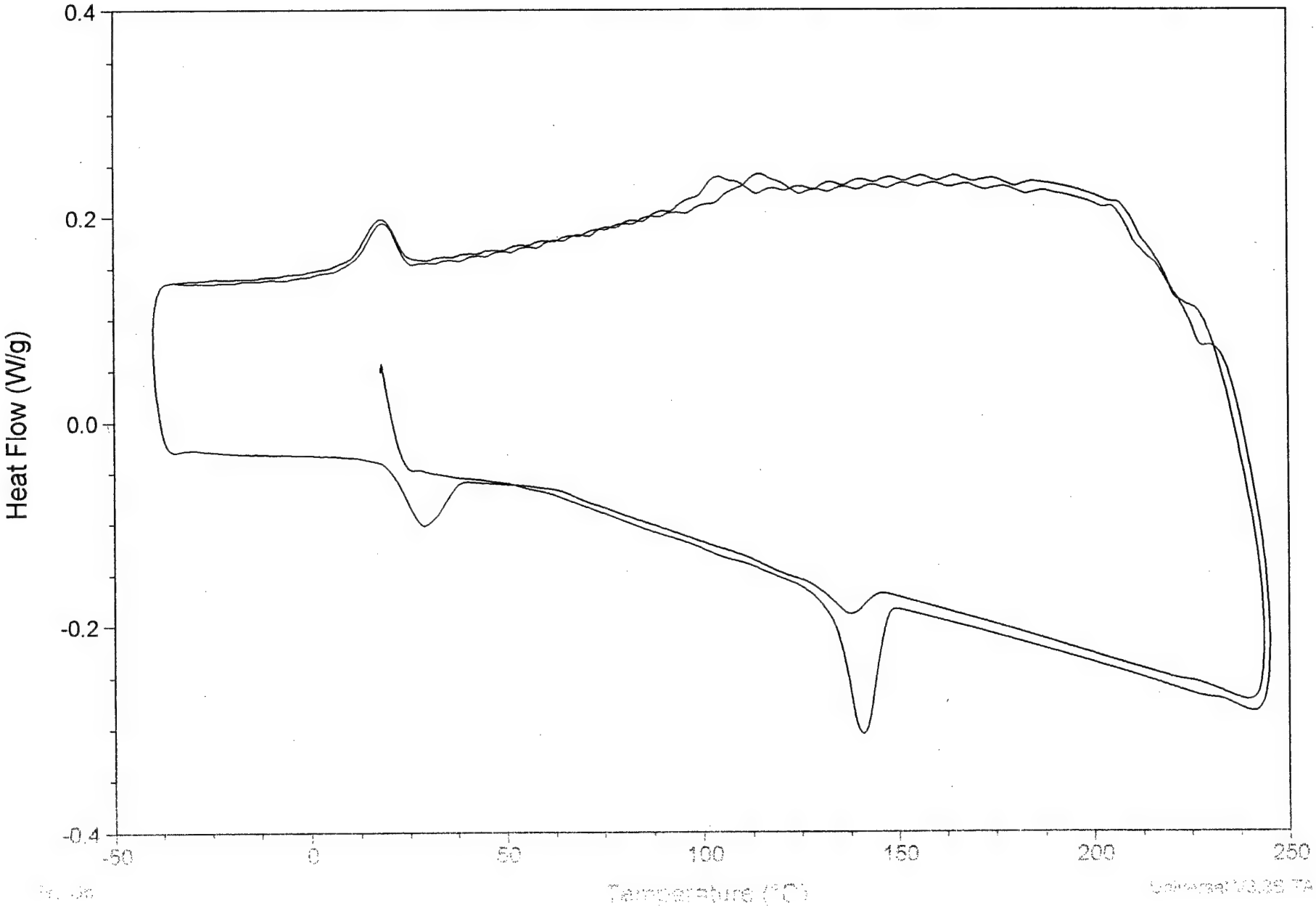
Crystal Structure of Perfluorinated POSS

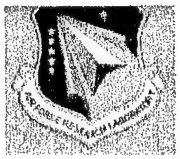


Sample: FluorodecylnTn
Size: 19.6700 mg
Method: heating 30 to 200 (20)
Comment: This is Joe Mabry's stuff

DSC

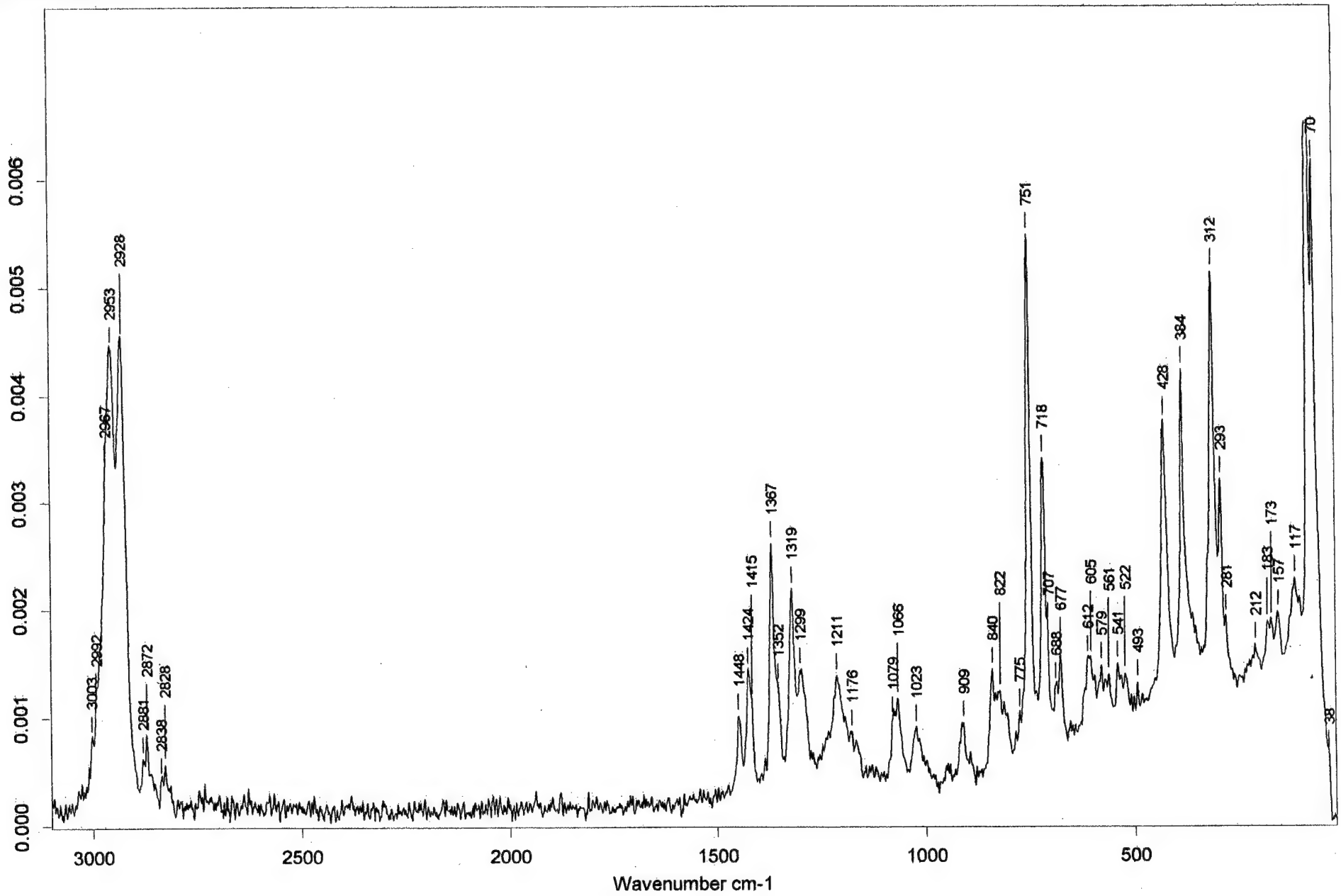
File: C:...\Patrick\MDSC\FluorodecylnTn.002
Operator: Patrick
Run Date: 21-Nov-02 07:26
Instrument: 2920 MDSC V2.4F





Sample: RLB-IV-26 fluorooctyl8T8
Sample Source: white powder
Laser Power : 600

Date Recorded: 24/02/2003
Time Recorded: 16:42:32



kerri_new
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HEDM/PRS
EQUINOX 55

Sample Scans 500
Raman Laser Wavenumber 9394

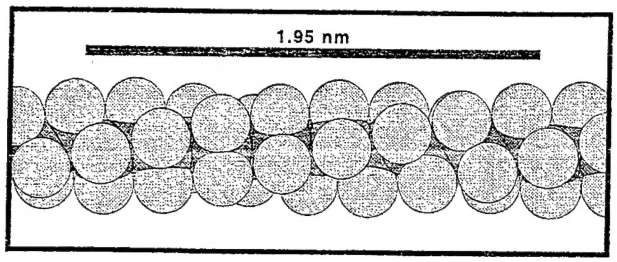

FIGURE 30.19. Polytetrafluorethylene (Form IV).

Polytetrafluoroethylene [-(CF_2)-] Form I (above 30 °C). Space group (hexagonal packing of helical chains of variable twist). Hexagonal approximation a=0.567 nm (35 °C) to 0.574 nm (218 °C). c=0.1300 nm per CF_2 group†. Cell volume=0.0362–0.0371 nm^3 per CF_2 group. Density =2290–2240 kg/m^3. Diffuse pattern with sharp $hk0$ reflections (hexagonal).

TABLE 30.11. *Polytetrafluoroethylene [-(CF_2)-] Form II (below 19 °C). Observed hk0 reflections.*[a]

d-value (nm)	2θ (deg) (λ=0.1542 nm)	Relative intensity
0.4866	18.23	vvs
0.2823	31.69	vs
0.2447	36.73	s
0.2414	37.24	m
0.1850	49.26	m
0.1828	49.88	m
0.1627	56.58	m

[a]Space group (approximate) P1 [C_1^1] (Complex structure with a regular helix of 2.1598 CF_2 units per turn). Orthogonal approximation; a=0.9649 nm; b=0.5648; and c=0.1300 nm per CF_2 group†. Cell volume=0.03542 nm^3 per CF_2 group. Density=2340 kg/m^3. (From Ref. 9.)

Polytetrafluoroethylene [-(CF_2)-] Form III (high pressure) Space group Pnam [D_{2h}^{16}]. a=0.75 nm; b=0.56 nm; and c=0.26 nm†. Cell volume=0.1092 nm^3. Density=3040 kg/m^3. Peaks attributed to a monoclinic phase are also observed. (From Ref. 10.)

TABLE 30.12. *Polytetrafluoroethylene [-(CF_2)-] Form IV (19–30 °C).*[a]

hkl	*d* value (nm)	2θ (deg) (λ=0.1542 nm)	Relative intensity
100	0.4902	18.10	vvs
110	0.2830	31.61	s
200	0.2451	36.67	s
210	0.1853	49.18	m
300	0.1634	56.30	m
220	0.1415	66.02	m
310	0.1359	69.09	m
107	0.2422	37.12	vs
108	0.2183	41.37	vs
117	0.1985	45.70	w
118	0.1847	49.34	w

[a]Space group (presumed) $P3_1$ or $P3_2$ [C_3^2 or C_3^3]; Rotational disorder of helical chains. Z=15(CF_2). a=0.566 nm and c=1.95 nm†. Cell volume=0.0541 nm^3. Density =2302 kg/m^3. (From Refs. 8, 9, 11 and 12.)

30.8 POLY(P-PHENYLENE TEREPHTHALAMIDE) (PTTA) [—(C═O)—(C_6H_4)—(C═O)—NH—($_6H_4$)—(NH)—]

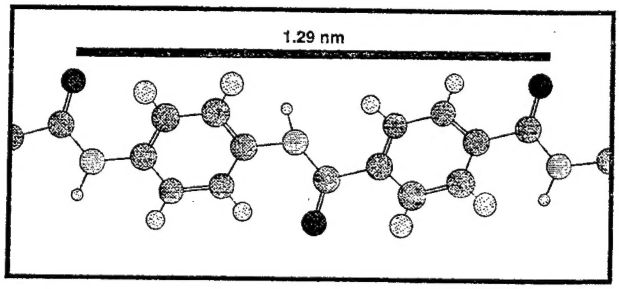

FIGURE 30.20. Poly(*p*-phenylene terephthalamide).

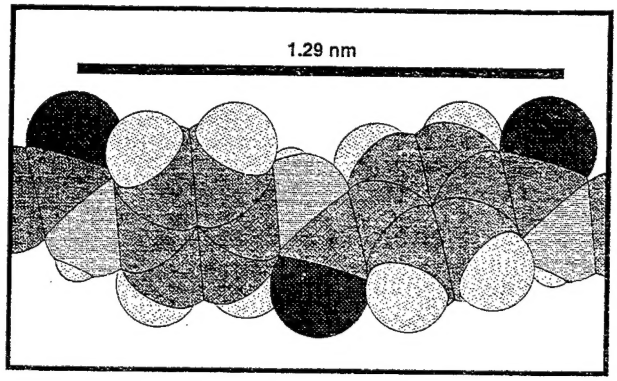

FIGURE 30.21. Poly (*p*-phenylene terephthalamide).

Linear Fluorocarbon Analogs

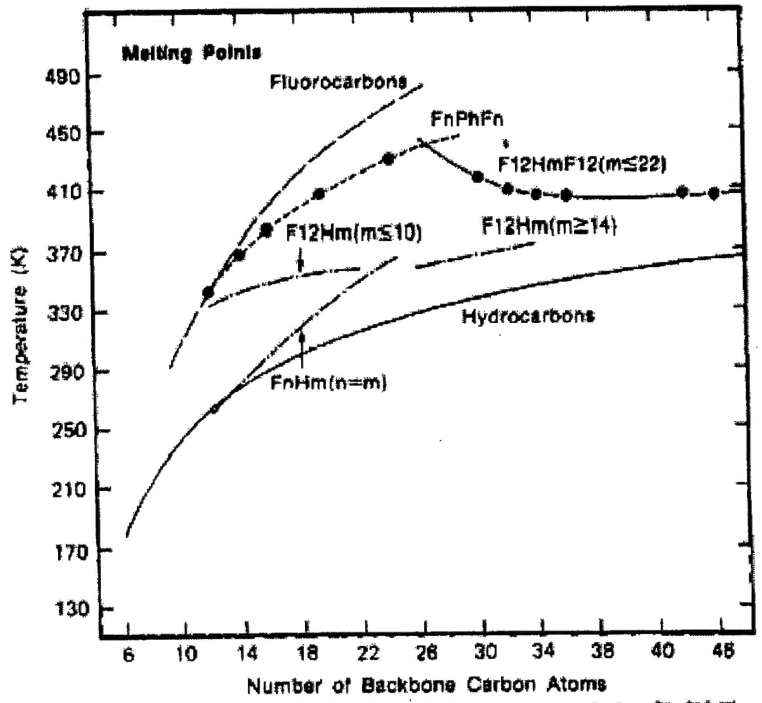

Figure 2. Comparison of the melting points of the **FnPhFn** triblocks with those of the *n*-alkanes, perfluoro-*n*-alkanes, and previously studied diblock and triblock materials.

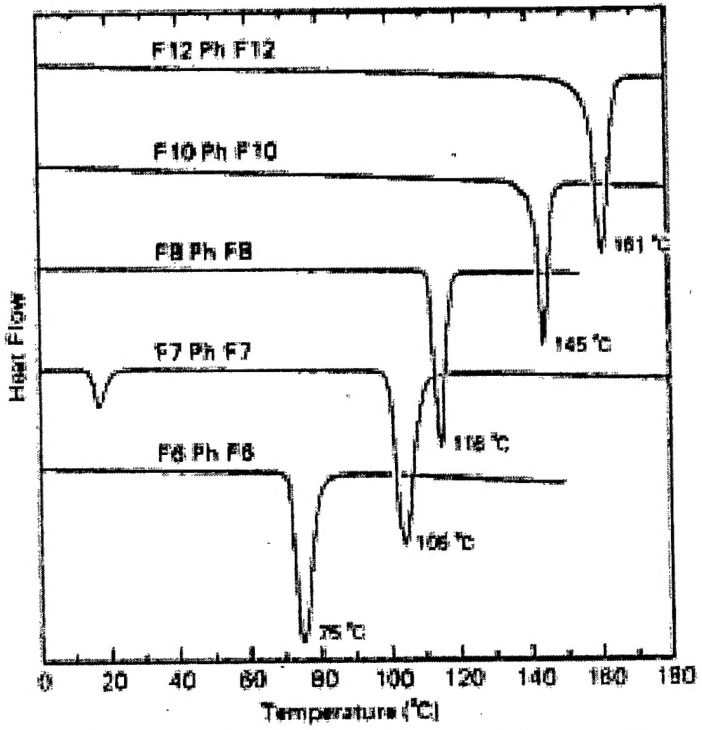

Figure 1. Differential scanning calorimetry thermograms of the **FnPhFn** triblocks. Temperatures refer to peak positions.

Tweig et. al.; Macromolecules **1991,24,** 3901-3905

Conclusions

- Fluorosubstituted POSS has unusual melting behavior-evidence of polymorphs
- Melting point much higher than the arm melting-consistent with "coupled" arm motions although Raman spectroscopy does not show strong evidence of a lattice mode
- Frustrated Crystallization due to steric effects?

- Interactions with Karl Christe will solve the puzzle

Acknowledgments

- AFOSR-Mike Berman
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